THE LIFETIME OF METASTABLY BOUND POLAR MOLECULES

A. K. GHOSH

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

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ABSTRACT. Lifetime of metastably bound double molecules in polar gases has been considered. The method applied is similar to the one-body theory of α-radioactivity. The results show that the metastable systems have usually a life-time which is long compared to the mean time between collisions. Consequently, metastably bound molecules have to be treated as stable bound molecules.

INTRODUCTION

The bound double molecules may be defined as two molecule systems for which the total energy is less than the energy of the separated molecules (Stogryn *et al*, 1959). However, depending on the energy of the system, there are bound systems which from the standpoint of quantum mechanics can dissociate only by leakage through the potential barrier. These systems are known as metastably bound double molecules. The consideration of dimers is necessary for a proper understanding of the equation of state in gases and also to interpret transport properties of dense gases. An important property of the metastable systems is its half-life for dissociation. If the collision time is short compared to half-life, then the metastable molecules behave like bound molecules and if the reverse is true they are to be treated as free molecules. For non-polar gases, Stogryn and Hirschfelder (1959) have considered the half-life of metastably bound molecules. As the intermolecular potential of polar molecules differs widely from that of non-polar ones due to the presence of long-range dipole forces, it is necessary to consider separately the half-life of metastably bound double molecues in polar gases. In this paper, a calculation of the half-life has been made for H_2S which is a typical polar molecule.

THEORETICAL FORMULATION AND CALCULATION

It is possible to calculate the half-life of metastable molecules by using the WKB approximation, the theory being very similar to the one body model theory of α-radioactivity (Bethe, 1937, Kemble, 1937, and Bohm, 1951). Following this procedure, the time period of vibration t can be written as (Stogryn *et al*, 1959),

$$t = 2\int_{r_1}^{r_2} \frac{dr}{\sqrt{2/\mu(K-\phi_{eff})}} \qquad \ldots (1)$$

where K is the initial relative kinetic energy or the total kinetic energy in the centre of mass coordinate system, μ the reduced mass of the molecules, r_1, r_2 the two turning points for a fixed value of K and Kb^2, and $\phi_{eff} = \phi(r)+Kb^2/r^2$, b being the impact parameter. Thus, the probability of dissociation per second, P, is given by,

$$P = \theta/t \qquad \ldots \quad (2)$$

where θ is the probability of transmission through the barrier and the mean life time τ is

$$\tau = \frac{1}{P} = t/\theta \qquad \ldots \quad (3)$$

Following the WKB method, the transmission coefficient, θ is given by,

$$\theta = e^{-2G}$$

where

$$G = \frac{1}{\hbar}\int_{r_2}^{r_3} \sqrt{2\mu(\phi_{eff}-K)}dr, \qquad (4)$$

r_2 and r_3 being the turning points inside and outside the potential well respectively. The WKB approximation is valid for $G > 1$.

For polar molecules the potential energy of interaction can be written as (Hirschfelder, *et al*, 1954),

$$\phi(r) = 4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6] - \frac{\mu^2}{r^3}\, g(\theta_1, \theta_2, \phi) \qquad (5)$$

$$g(\theta_1, \theta_2, \phi) = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi$$

where θ_1, θ_2 are the angles of inclination of dipoles (dipole moment μ) to the line joining the centres of the molecules and ϕ is the azimuthal angle. For $\mu \to 0$, Eq. (5) reduces to the well known Lennard-Jones (12:6) potential for non-polar gases. For any particular relative orientation of the dipoles a numerical value can be assigned to $g(\theta_1, \theta_2, \phi)$ i.e. eq. (5) becomes,

$$\phi(r) = 4\epsilon[\sigma/r)^{12}-(\sigma/r)^6] - \frac{A\mu^2}{} \qquad (6)$$

Let us define the following reduced quantities,

$$\phi^* = \phi/\epsilon,\ K^* = K/\epsilon \text{ and } b^* = b/\sigma$$

Then we have,

$$\phi_{eff}^* = 4y^6 - 4y^3 - 4A^* y^{3/2} + K^* b^{*2} y, \qquad (7)$$

where $y = r^{*-2}$ and $A^* = \frac{A\mu^2}{4\epsilon\sigma^3}$

Consequently,

$$t = h/2\epsilon\Lambda^* \int_{y_2}^{y_1} dy/[y^{3/2}(K^* - 4y^6 + 4y^3 + 4A^* y^{3/2} - K^* b^{*2} y)^{\frac{1}{2}}] \quad \ldots (8)$$

and

$$G = \pi/\Lambda^* \int_{y_3}^{y_2} \frac{(4y^6 - 4y^3 - 4A^* y^{3/2} + K^* b^{*2} y - K^*)^{\frac{1}{2}}}{y^{3/2}} dy \quad (9)$$

where Λ^* is the reduced de Broglie wavelength of the molecules given by $\Lambda^* = h/\sigma\sqrt{m\epsilon}$ with σ, ϵ having usual significance.

The hyper-elliptic integrals in the right hand side of eqs. (8) and (9) were evaluated numerically. The limits of the integrals and the values of the integrals at the limiting points were obtained by the method described by Stogryn and Hirschfelder (1959).

TABLE I

Lifetime for metastably bound double molecules of H_2S

K^*b^{*2}	K^*	$\Lambda^* G/\pi$	$2\epsilon\Lambda^* t/h$	τ_{H_2S} (sec)
	0.03	1.455	9.19	2.47×10^{8}
1.5734	0.06	0.615	13.47	6.21×10^{-3}
	0.09	0.130	26.45	2.29×10^{-9}
	0.10	2.810	1.40	1.60×10^{27}
	0.20	1.581	1.63	1.79×10^{10}
3.1486	0.30	0.903	2.14	9.48
	0.40	0.404	2.45	1.31×10^{-6}
	0.98	0.137	1.18	1.30×10^{-10}
4.4382	1.00	0.081	2.32	4.22×10^{-10}
	1.02*	0.033	6.79	2.70×10^{-11}

*G value for $K^* = 1.02$ is less than 1. Thus, WBK method does not hold for it.

In order to make sample calculation for H_2S it was assumed that the dipoles were in the head-to-tail position which corresponds to $A^* = 0.529$. For this potential the force constants have been obtained by Itean *et al*, (1961) and they are : $\sigma = 4.034$ Å; $\epsilon/k = 88.4$°K and $\Lambda^* = 0.197$. The integrals were evaluated for three fixed values of K^*b^{*2} and several values of K^*. The potential energy curves corresponding to K^*b^{*2} values are shown in Fig. 1. The values of τ thus obtained for H_2S are given in Table I.

The mean time between collisions is of the order of 10^{-9} or 10^{-10} secs. at N.T.P. A comparison with the results obtained for Argon by Stogryn and Hirschfelder

(1959) shows that the lifetime for metastably bound double molecules for a polar gas is much larger than for a non-polar gas. This result is expected due to the presence of long-range dipole-dipole force in polar gases which is generally attrac-

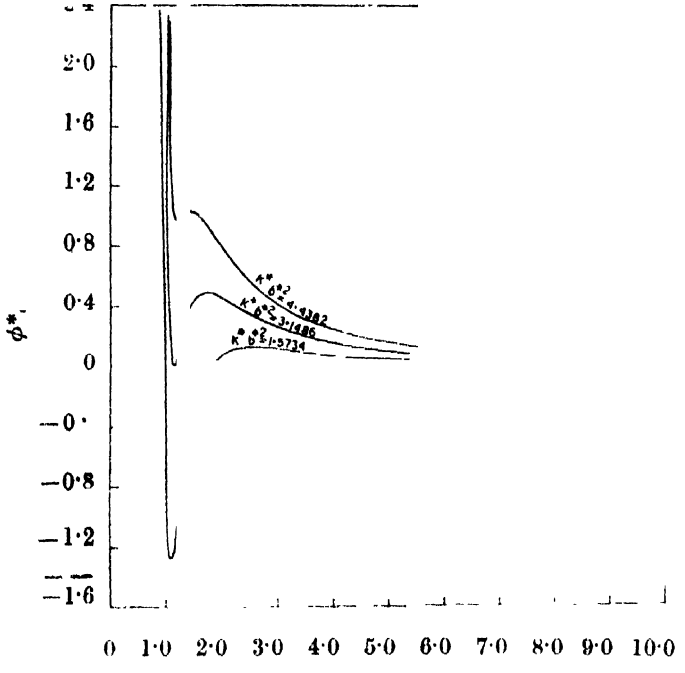

Fig. 1. Effective potential energy curves for H_2S.

tive. Thus except at very high energies the metastably bound molecules behave as stable molecules for polar gases. Consequently, the effect of metastable systems will be more in polar gases than in non-polar gases.

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